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X63-11356

NASA TT F-8288

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FACILITY FORM 602	N71-71164	
	(ACCESSION NUMBER)	(THRU)
	10	None
	(PAGES)	(CODE)
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON November 1962

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OXYGEN ELECTRODES FOR A HIGH-TEMPERATURE FUEL CELL* (I)

by

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1. INTRODUCTION

High-temperature fuel cells are used at 400 - 800°C. The electrolyte is a molten salt, the major component of which is an alkali metal carbonate. The gas electrodes are made of porous metal. Oxygen (or air) and a fuel gas (hydrogen, carbon monoxide) are supplied to the cathode and anode respectively. The fuel gas is oxidized electrochemically, thus generating electricity.

Earlier studies¹⁻³⁾ on high-temperature fuel cells have been concerned with the preparation of porous gas electrodes and the major points of interest have been 1) lower polarization, 2) higher current densities, 3) longer life, and 4) higher efficiency.

Broers showed experimentally¹⁾ that polarization was reduced when carbon dioxide was mixed with the oxidizing gas (oxygen or air). Chambers and Tantram²⁾ showed that the potential of the oxygen electrode in the alkali carbonate was also affected by the partial pressure of carbon dioxide. The influence of the CO₂ to O₂ ratio on the polarization has not been investigated fully, however.

In order to study the reaction mechanisms at the electrodes of high-temperature fuel cells, we carried out a few preliminary experiments on the characteristics of the cells, using simple cells which gave reproducible results. We used wires or plates of silver, platinum and other metals, and studied the effects of gas composition, temperatures, etc., on the reaction at the cathode ($\text{CO}_2 + 1/2 \text{O}_2 + 2\text{e} \rightarrow \text{CO}_3^{2-}$).

2. Gas Electrodes and the Capillary Rise of Molten Salts

It is generally thought^{4, 5)} that the reactions at the electrodes take place at the site where the three phases, namely electrode, the gases, and the liquid electrolyte, meet. We tested three electrodes (Fig. 1) which generated a fairly large amount of electricity and had good reproducibility.

* Reported at the 14th annual meeting of the Japanese Chemical Society, April 3, 1961.

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The matrix type a is a modification of Proers' electrode¹⁾. We prepared our electrodes by immersing porous silica - alumina plates (porosity 40 - 50%) in the fused salts. The pretreated plates were placed in a crucible containing the fused salts, the salt surface was covered with metal powder (Ag, etc.) and a metallic mesh (Ni), and the whole assembly was fastened to a copper tube.

Electrode b is a modification of the one used by Douglas⁶⁾; a metal tube was equipped with a porous Ni plate (porosity 80%, thickness 0.2 - 0.4 cm) at one end.

Electrode c is a metal plate, or a wire with a zigzag end, which dips into the electrolyte.

We were unable to obtain a constant output of electricity from electrodes a or b. The reason for this was that, because of its great surface tension, the electrolyte covered the entire metallic surface. The IR drop was considerable in a, while a pressure of 30 - 50 mm Hg was required to force the gas through the electrode b, and therefore it was impossible to generate electricity at a constant rate in either case.

The area of three-phase region was very small in electrode c, particularly with the plate electrode; therefore we did not expect good results. To our surprise, the rate of generation of electricity was considerable. Thus, electrodes of this type were used in the experiments.

The fused electrolyte used throughout the work was a mixed alkali metal carbonate (Li_2CO_3 , Na_2CO_3 and K_2CO_3 , molar ratio 4 : 3 : 3), which melts at 400° C and is chemically stable up to 900° C^{6, 7)}.

The capillary rise of the fused salts was determined as follows. Two nickel-plated iron plates were assembled in a V (Fig. 2) and fastened with Ni wire. The vee was immersed in the fused salt and left to stand for 2 - 3 minutes; it was then removed and washed with cold water. The area that came into contact with the fused salt became passive to oxidation and thus retained a metallic luster, while the other area was rapidly oxidized and became blue or black. The experiments were carried out over the temperature range from 400 - 900° C, but the results were practically the same. Therefore only the data at 700° C are given (Fig. 2). It is seen that the surface rose more than 10 mm when the separation between two plates were 1 mm and was several millimeters even when the distance was 2 mm. The surface tension of the mixed salt (eutectic mixture of Li_2CO_3 and Na_2CO_3) is 225 dynes/cm⁴⁾ at 550° C, i.e., approximately three times that of water. Since the surface tension is so great, it is essential to have a limited amount of electrolyte in the matrix in order to avoid excessive coverage of the electrodes (drowning or flooding) by the solution at ambient pressure. No electricity is generated if an excess of solution is present, as was the case in Broers' and Chambers' experiments.

3. Experimental Procedure

The polarization characteristics were determined with the apparatus illustrated in Fig. 3. Forty grams of mixed alkali metal carbonates (about 1.6 cm deep when fused) was placed in a silver crucible (diameter 4 cm;

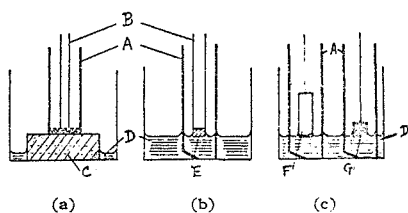


Fig. 1. Electrodes: (a) Matrix type; (b) Porous metal type; (c) Metal plate or wire.

A) sintered aluminum tube; B) metal tube; C) matrix containing fused salts; D) fused salts; E) porous Ni electrode; F) metal plate (Ag, Pt, Ni); G) metal wire (0.2 - 0.3 mm in diameter) with one end bent

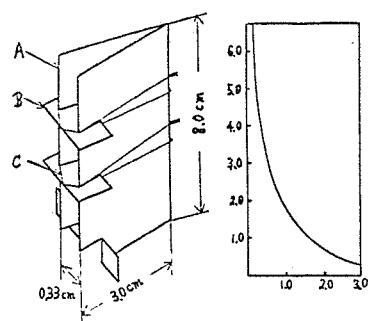


Fig. 2. Capillary rise of fused salts. Left: A) Ni-plated Fe plate; B) fixed plate; C) Ni wire. Right: Ordinate: Height of the surface of the solution (cm); Abscissa: Distance between plates (mm)

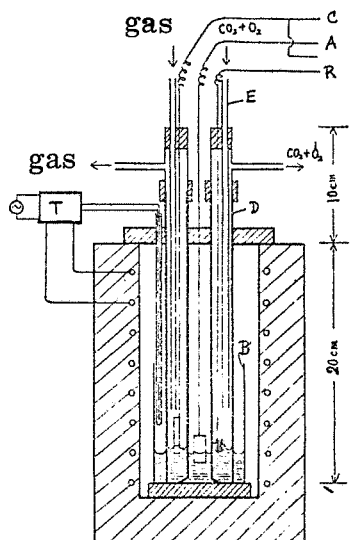


Fig. 3. Apparatus for gas measurements: A) anode; B) silver crucible; C) cathode; D) aluminum tube; E) metal tube (Ni-plated Cu); R) supplementary electrode; T) automatic photoelectric thermo regulator

depth 12 cm), and the crucible was placed in an electric furnace. The temperature of the furnace was kept constant within $\pm 2^\circ\text{C}$ by means of an automatic photoelectric thermo regulator. Into the melted salt in the crucible were placed an anode, a cathode, and a supplementary electrode (counterelectrode) separately contained in a sintered alumina tube (12 mm ID, 14 mm OD), with the lower ends dipping in the melt. Two types of cathode were employed, namely rectangular platinum or silver plates (1.0×5 cm), with a fused-on platinum lead, and platinum or silver wires (0.2 - 0.3 mm diameter) one end of which was bent 90 times in a zigzag manner. A platinum plate was used as the anode, and a silver wire with a zigzag end as the supplementary electrode. The flow rate of the mixed gas (CO_2 and O_2 , 1 : 1) was 8 ml/min. The mixture of CO_2 and O_2 , with various volume ratios of N_2 , was sent to the cathode, and a constant electric current was produced between the anode and cathode. The polarization of the electrodes was determined with a vacuum-tube voltmeter. The gases were supplied at a constant rate from glass bottles by replacing the gas with water. Contamination of the water with CO_2 was avoided by covering the surface of the water with a thin layer of paraffin oil. The silver wire used as the supplementary electrode slowly dissolved in the solution. The dissolution was particularly fast at the surface of the electrolyte. The reason for this was not clear. The electrode dissolved even when no electricity was generated. Above 400°C , both silver oxide and carbonate should have been decomposed and reduced to metallic silver; therefore it was possible that the silver did not enter the melt in the form of the silver ion.

4. Experimental Results and Discussion

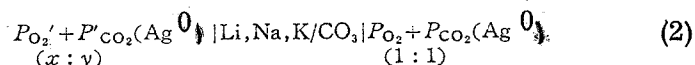
(i) Effect of gas composition

The reaction that takes place at the cathode of high-temperature fuel cell may be represented as



Therefore, the gas composition should affect the polarization characteristics. (Here we introduce the notation P_{O_2} and P_{CO_2} , the partial pressures of oxygen and carbon dioxide.) First, the potential of the cell described below was determined at 600°C , varying the partial pressures of oxygen and carbon dioxide (P'_{O_2} , P'_{CO_2}) at one electrode while maintaining the partial pressures (P_{O_2} , P_{CO_2}) at a constant one-to-one ratio at the other electrode.

We used silver wire, 0.3 mm in diameter, with one end bent in 90 zigzag folds. The system can be represented simply as



The potential of this cell is given by the equation

$$E = -\frac{RT}{4F} \ln \frac{P'_{\text{O}_2}}{P_{\text{O}_2}} - \frac{RT}{2F} \ln \frac{P'_{\text{CO}_2}}{P_{\text{CO}_2}}$$

The experimental results agreed well with the above equation. That is, when the ratio of P'_{O_2} to P'_{CO_2} ($x : y$) was 1 : 1, the potential was zero; this potential was positive whenever the ratio of partial pressures became either greater or less than unity. Analogous results were obtained when the silver

wire of the left electrode in cell (2) was replaced by platinum. The potential, however, was 30 - 50 mv lower in the latter case with the same gas composition. From the above results, we concluded, in agreement with others²⁾, that both O_2 and CO_2 participate in the cathode reaction, as indicated by Eq. 1.

The polarization characteristics were studied at 600°C using, as above, Pt wire and changing the ratio of O_2 to CO_2 . The results are given in Fig. 4 and the table. It was found that the polarization was extremely high when either O_2 or CO_2 was used alone, and only 2 - 3 ma could be generated. The polarization was only 0.3 v, however, even when 50 ma was generated, if the gas composition lay in the range of 30 - 80% O_2 . According to Eq. (1), the reaction should take place between one mole of oxygen and two moles of carbon dioxide, that is, 33% oxygen. This gas composition corresponds to curve 8 of Fig. 4. Thus, we concluded that both O_2 and CO_2 participated in the electrode reaction.

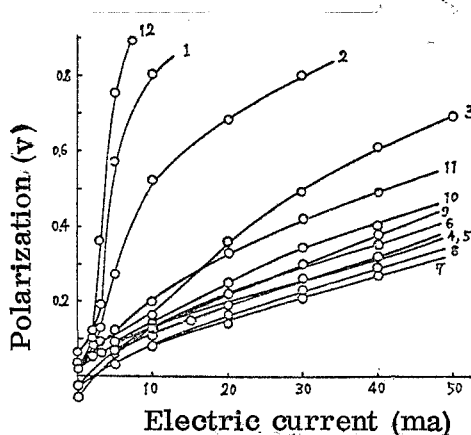


Fig. 4. Polarization characteristics of $O_2 + CO_2$
(x : y)/Pt wire electrode at 600°C

Partial pressure of O_2			
1	1.00	7	0.40
2	0.95	8	0.33
3	0.90	9	0.20
4	0.80	10	0.10
5	0.60	11	0.05
6	0.50	12	0.00

The above-described cell was used throughout the following experiments because polarization was very small, and the cell was highly reliable.

The following equilibrium occurs in alkali metal carbonate melts:



The equilibrium shifts to right with rise of temperature⁸⁾. It is known⁹⁾ that Pt (O₂) works as an oxygen electrode ($2\text{O}^{2-} \rightleftharpoons \text{O}_2 + 4\text{e}$) in both alkali metal carbonate and alkali metal sulfate melts. For the above reasons, the reactions at the electrode which we have formulated as Eq. 1 must be more complex, and thus more detailed studies will have to be made.

(ii) Effect of temperature

The effect of temperature on polarization was studied, using the same Ag electrode and the same gas composition (O₂ = CO₂, 1 : 1). The results are shown in Fig. 5. Polarization decreased with rise of temperature. However, the degree of polarization did not change greatly above 700 - 750° C.

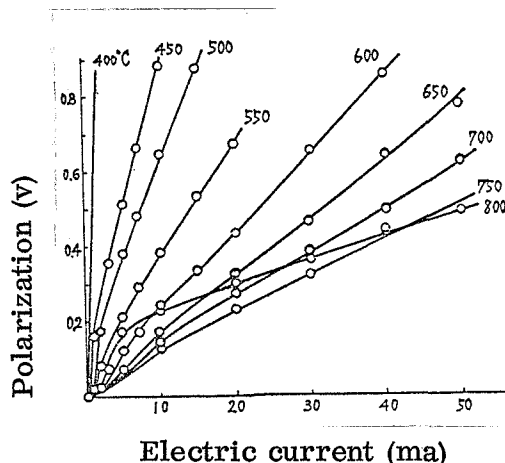


Fig. 5. Effect of temperature on the polarization characteristics of O₂ + CO₂ (1 : 1)/Ag wire electrode

The activation energy can be calculated from the following equation:

$$\left(\frac{\partial \ln i}{\partial T} \right)_\eta = \frac{A H}{R T^2} \quad \text{or} \quad \log i = - \frac{A H}{2.3 R T} + C$$

Values of log *i* were plotted against 1/*T* for the polarization (η) at 0.1, 0.3 and 0.5 v. The experimental points followed a straight line, except in the temperature range 750 - 800° C. The activation energy was calculated from the slope of the line. It was equal to 13.8 kcal/mole for $\eta = 0.1, 0.3$ and 0.5 v; that is, it was independent of polarization. The above value is close to the activation energy (10 kcal/mole⁷⁾) of the oxygen-generating reaction at the Pt electrode ($\text{CO}_3^{2-} \longrightarrow \text{CO}_2 + \text{O} + 2\text{e}$) in the electrolysis of alkali metal carbonates. This is the reverse of Eq. (1).

(iii) Polarization characteristics of plate electrodes

It was possible that the inside of the zigzag wire electrode was filled up with the electrolyte due to the capillary action and that, therefore, the reaction took place only on the outside surface of the electrode. Since the effective surface area was thus very difficult to measure, we carried out similar experiments, using a rectangular metallic plate (width 1 cm, thickness 0.3 - 0.5 mm) as the electrode. Only the bottom of the plate was in contact with the electrolyte solution. The results are shown in Figs. 6 and 7. The IR values were calculated from the distance between the supplementary electrode and the cathode, assuming that the specific resistance of the electrolyte was 0.8 ohm-cm. The decrease in the IR values obtained by the commutator method was in fairly good agreement with the above value. It can also be seen from Fig. 6 that practically no electricity was generated when nitrogen was used to dilute the $O_2 + CO_2$ mixture.

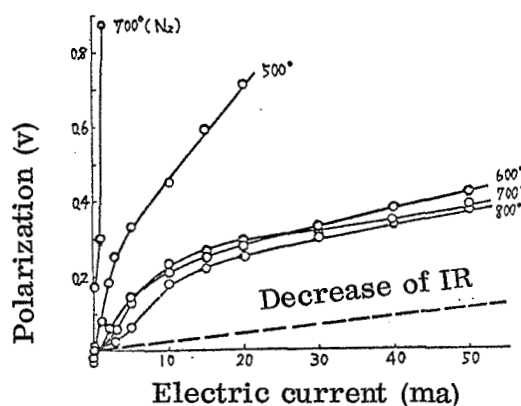


Fig. 6. Polarization characteristics of $O_2 + CO_2$ (1 : 1)/Ag plate electrode

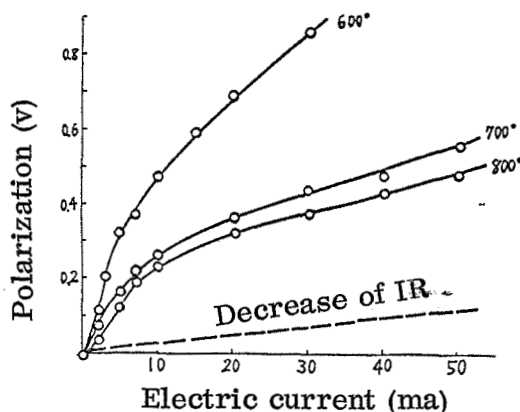


Fig. 7. Polarization characteristics of $O_2 + CO_2$ (1 : 1)/Pt plate electrode

These results show that a considerable electric current can be obtained when metallic plates are used as the electrodes, even though their effective surface area, the area where the three phases are in contact, is small. The significance of the experiments using plate electrodes, in contrast to the metallic wire electrodes, is that the polarization is considerable for currents less than 10 ma and the IR value decreases. Our being able to obtain a fairly large electric current using these simple electrodes indicates that they may be useful for investigating the most important problems related to high-temperature fuel cells: the physicochemical structure of the three-phase region, the effects of the dispersion of gas through the metal, etc.

5. SUMMARY

A few experiments were carried out to ascertain which electrodes could best be employed in investigating the reaction mechanism at the electrodes of high-temperature fuel cells. The effects of temperature and gas composition on the polarization characteristics of the oxygen electrode were also investigated.

1. The polarization was approximately 300 - 400 mv at 600 - 800° C, and a fairly large current was obtained when a rectangular metallic plate (Ag or Pt, width 1 cm) was used as the electrode and the CO₂ - O₂ mixture was passed along these electrodes through the electrolyte (mixture of alkali metal carbonates).

2. The effect of the gas composition was investigated using wire electrodes with one end bent in a series of folds. It was found that both O₂ and CO₂ participated in the reaction when a mixture of them was used. The polarization was small for oxygen contents from 30 - 80% and became significant at other concentrations.

3. The effect of temperature was investigated, using silver electrodes and a 1 : 1 mixture of CO₂ and O₂. It was found that the polarization decreased with increase of temperature and that it did not change significantly above 700° C.

A part of the expense of the present investigation was supported by the Scientific Research Foundation of the Ministry of Education, to which we wish to express our gratitude.

(Received April 19, 1961)

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